

## REMARKS

Applicant respectfully requests reexamination, reconsideration and allowance of this application, including the final rejection of claims 1-43, as amended, in view of the interview on January 6, 2005 noted below, and the following. Entry of the foregoing amendment is respectfully requested.

Applicant acknowledges the kindness of Examiner Jeffrey C. Mullis in the interview with the undersigned, Applicant Mitsu Shida, and Mark Pucci held at Mr. Mullis' office on January 6, 2005 from approximately 12:30 p.m. to approximately 1:30 p.m. At the interview, Applicant's Attorney presented a proposed Amendment B After Final Under 37 CFR 1.116, substantially the same as this Amendment B, an Affidavit of Mark Stephen Pucci identical to the Affidavit of Dr. Pucci filed herewith, and multilayer film samples as examples of applications which use the type of adhesives that this application is directed to. Amendment B as presented to Examiner Mullis sought to amend claims 1 and 14 to recite in step b. "mixing with shear mixing, in the absence of cross-linking material, at least 50% by weight of the polyolefin-based adhesive resin of the polymerization product." Following discussion of the proposed amendment, the rejections based on Schombourg et al. Patent No. 6,448,343 ("the '343 patent") and consideration of the Affidavit of Dr. Pucci, it was proposed to amend claims 1 and 14 to recite "mixing while avoiding cross-linking" and "at least 50% by weight based on the polyolefin-based adhesive." During discussion, the original wording proposed was "mixing while minimizing cross-linking", which was accepted by Examiner Mullis. Therefore, we are using the expression "minimizing cross-linking" in our amended

claims. As stated in the Interview Summary prepared by Examiner Mullis at the interview, it was his position that since the '343 patent states cross-linking is desirable and utilizes lower amounts of polyolefin "a", the above proposed amendment probably would overcome the rejections based on the '343 patent. However, Examiner Mullis suggested that an RCE should be filed since further consideration, and possibly a search, would be needed regarding limitations newly added to the claims.

### ***Applicant's Claimed Process and Product***

Applicant has discovered that an improved polyolefin-based adhesive resin with less imperfections, such as gelled polymer, can be obtained by reducing the number of melt processing and extrusion steps after polymerization of the olefin monomer or co-monomer, and, as conventional in such polyolefin-based adhesive resins, avoiding cross-linking. Gelled polymer results from both cross-linking and from the steps of melt processing and extruding. Applicant's process and product are distinguished from processes for producing materials that intentionally cross-link, such as that of Schombourg et al., which require the presence of cross-linking material during mixing. Schombourg et al teaches a process for producing silane vulcanized thermoplastic elastomers, in which aminosilanes are present to achieve cross-linking. In regards to adhesive properties, Schombourg et al's elastomers do not have the adhesive properties of the polyolefin-based adhesive resins that this application is directed to, and are not usable as adhesives for bonding to dissimilar materials, per se. The Examiner is correct that the material described in Schombourg may have adhesive properties when used to bond to materials of identical composition. However, the

material described in Schombourg will not adhere to dissimilar materials such as polyamides, polyvinyl alcohol, ethylene vinyl alcohol copolymer, metals, glass, wood, and paper, as described in Applicant's claims 30, 34, and 38. The true value of the material described by the Applicant is that it bonds to materials that are both similar **and** dissimilar in composition, and therefore can bond dissimilar substrates to one another in important commercial processes such as coextrusion as described in claims 32, 36, and 40.

#### ***Amendment of the Specification***

Applicant recently noted an inadvertent typographical error in a patent number in the **Background of the Invention** section of the Specification in Paragraph [0006] on page 2, 2nd line from the bottom of the page. The number "4,478,885" should have appeared as --4,487,885--. It is noted that the former number does not represent a patent issued on November 11, 1984, and is not related to the subject matter of Applicant's instant application. The correct number, --4,487,885--, appears in the Specification, in the **Summary of the Invention** in Paragraph [0019] at the top of page 7, 2<sup>nd</sup> line, and in the **Information Disclosure Statement** in this case filed by Applicant on October 6, 2003, and references a patent issued to Adur, et al. on November 11, 1984. In view of the obvious inadvertent typographical error in the number, and in view of the correct number appearing elsewhere in the Specification and in the Information Disclosure Statement, Applicant respectfully requests entry of the amendment to the Specification.

## ***Amendment of the Claims***

### **Cross-linking is detrimental in Applicant's Product and Process**

In his response of August 8, 2004 to the Office Action of May 11, 2004, Applicant pointed out that in his claimed process and product cross-linking is detrimental and is to be avoided, whereas the primary reference, Schombourg et al. teaches that cross-linking is necessary and a cross-linking material is an essential ingredient. (Schombourg et al. Col. 2, lines 61-62 and all claims). In the Office Action of November 4, 2004, in reply to this point, the Examiner stated that "there is nothing in [Applicant's] claims excluding cross-linkers or cross-linking properties."

While Applicant submits that the absence of cross-linking is inherent in his claimed process in order to produce the adhesive resins, to clarify the invention in his claims, Applicant, in the present amendment, has amended the claims to recite that cross-linking is minimized. The recital that cross-linking material is minimized during mixing is consistent with the statement in the specification at Para. 0022. It is respectfully submitted that Applicant's claims 1-40 now clearly distinguish Applicant's process and product from the process and product of Schombourg et al. Applicant notes that Schombourg et al., teaches that an aminosilane is an essential ingredient during mixing, and that the aminosilane crosslinks with the anhydride (Col. 3, line 16). Therefore, the primary reference fails to teach, disclose or suggest every element of Applicant's claims as required under 35 USC 102(e).

Regarding the rejection of claims 41-43 under 35 USC 103(a), the rejection is grounded on Schombourg et al's purported teaching of use of his elastomer as an adhesive. (Office Action of May 11, 2004, Page 5, 2<sup>nd</sup> sentence). However, Applicant

has shown in Amendment A, filed August 6, 2004, that Schombourg et al. does not teach that the elastomer can be used as an adhesive to dissimilar materials per se, but only that it may be used as an ingredient in an adhesive composition. (Schombourg et al. Col. 8, line 6). Applicant respectfully submits that there is no support for the conclusion that "Schombourg et al. discloses that his composition should be used as an adhesive." That Schombourg et al.'s elastomers are not adhesives as produced or of the type produced by Applicant's claimed method is set forth in the Affidavit of Mark Pucci submitted with this Amendment. Therefore it is submitted that the premise of the rejection and the alleged motivation as stated by the Examiner are also without support. Thus, the rejection must fail for lack of support.

**Applicant's claimed process requires a major amount of polyolefins**

Applicant's claims require the presence of a polymerized olefin or olefins. Note that the claims state in step b. that "the polymerization product [of step a., polymerizing a monomer of at least one olefin, is] mixed ..." Thus the polymerization product of step a. must be present. The Examiner appears to assert that the claims are not limited to the amount of polyolefin in the adhesive composition (Office Action of November 4, 2004, page 3, last three lines). To further clarify that polyolefin is a major component of his process and product, Applicant has amended the claims to recite that the polymerization product of step a. comprises at least 50% by weight of the adhesive resin. That the polyolefin constitutes at least 50% by weight of the adhesive is supported by the Specification at Para. 0026, the last two lines on page 9.

***Applicant's Claims Not Related to Ordinary Thermoplastic  
Material Which Becomes Sticky When Molten***

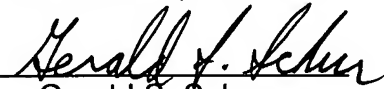
In the Action of November 4, 2004, the Examiner states the position that any thermoplastic material when molten is generally sticky "and would at least be expected to bond to an identical thermoplastic composition". As previously mentioned, Applicant's polyolefin-based adhesive resin produced by his claimed process not only bonds to the same or similar materials, but to dissimilar materials such as metals, glass, wood and/or paper, and other substrates as stated in his Specification in Paragraph [0023] and in claims 30, 34, and 38. As heretofore noted, and as shown in Dr. Pucci's Affidavit, Schombourg et al's silane vulcanized thermoplastic elastomers do not have the adhesive properties of adhering dissimilar materials as does Applicant's claimed adhesives.

***Conclusion***

Entry of the above amendments is respectfully requested to place the application in condition for allowance. In view of the amendments and the above remarks, Applicant respectfully submits that upon entry of the amendments the claims are now allowable, and requests withdrawal of the rejections, and allowance of the application.

Respectfully submitted,

WELSH & KATZ, LTD.

By   
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**AFFIDAVIT OF MARK STEPHEN PUCCI**

Commissioner of Patents and Trademarks  
ATTENTION: Assistant Commissioner for Patents  
Washington, D.C. 20231

Dear Sir:

This affidavit is being filed in response to the Office Action mailed November 4, 2004, in regards to patent application 10/612,031.

I, MARK STEPHEN PUCCI, declare:

1. From 1995 to the present, I have been Vice-President of MSI Technology, 3930 Ventura Drive, Suite 355, Arlington Heights, Illinois, 60004. MSI Technology is the assignee of the above-identified patent application.
2. I obtained a Bachelor of Science in Biology in 1974 from Loyola University, Chicago, IL; a Bachelor of Science in Chemistry in 1976 from Benedictine College, Lisle, IL; and a Doctor of Philosophy in Material Science and Engineering in 1981 from Northwestern University, Evanston, IL.
3. Since 1980 I have been involved in industrial applications of, and research with, polymer materials, polymer processing, and polymer adhesives. I am co-author of approximately 25 abstracts, patents, articles, books, or papers relating to polymer materials, polymer processing, and polymer adhesives.
4. I have carefully reviewed the Office Action November 4, 2004, in the above-identified patent application, and my response is as follows.

The Examiner in the final Office Action argues that *"the limitation of adhesive property required by the claims would reasonably be met by any thermoplastic material given that a melted thermoplastic is generally sticky and would at least be expected to bond to an identical thermoplastic composition which was in the solid*

*state given that an identical thermoplastic composition would be compatible".*

However, the type of adhesive that this application is directed to is one where the compositions that are bonded to are often dissimilar in nature, and therefore require reactive sites, such as maleic anhydride, for the purpose of attaining adhesion to such dissimilar compositions. Such adhesives are well known and well established in the industry. These adhesives, often referred to as "tie layer adhesives" are commonly used for bonding together substrates that include polyolefins, nylon, ethylene vinyl alcohol copolymer (EVOH), metal and paper. For example, D. Zimmerman, in a published technical paper<sup>1</sup>, given in exhibit A, states:

*"Tie layer resins are chemically modified polyolefins used in coextrusion or coating operations to bond two dissimilar materials together that otherwise would have poor adhesion to each other"*

The Zimmerman paper further states that:

*"Anhydride modified polyolefins and ethylene copolymers are capable of chemically reacting with nylon, paper, some metals, and EVOH to provide excellent adhesion"*

Such adhesives are used for a variety of applications, many being multilayer packaging applications. Exhibit B shows a product publication by Mitsui Chemicals for their Admer® adhesive product line, which illustrates examples of these applications. These include multilayer bottles, films, tubes and trays for various packaging applications. Further reference to this type of adhesive can be found in the patents given as reference in this patent application.

The type of adhesives that this application is directed to rely on polar chemical groups that are grafted onto polyolefin chain backbones for obtaining adhesive bonding. The chemistry of this type of bonding is well known and widely published. For example, DuPont, in their product brochure for their Bynel® adhesives<sup>2</sup>,

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<sup>1</sup> 1999 Tappi Polymers, Laminations & Coatings Conference Proceedings

<sup>2</sup> DuPont product brochure, circa 1990



describes how the maleic anhydride polar chemical group used in their adhesives forms chemical bonding. This product brochure, given as exhibit C, shows the following reactions:

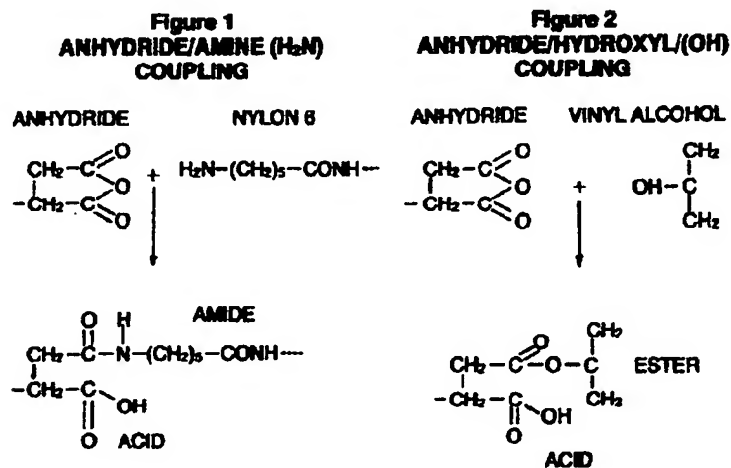


Figure 1 above shows the direct reaction of the maleic anhydride group in the adhesive with the amine group of a nylon substrate to form an "amide" adhesive bond between the two compositions. Figure 2 above shows the direct reaction the maleic anhydride group with the hydroxyl group of an EVOH substrate to form an "ester" adhesive bond between the two compositions.

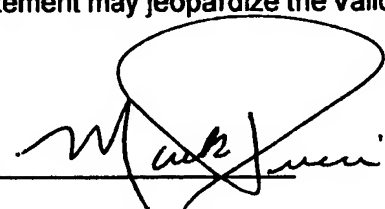
Similar illustrations of this maleic anhydride bond formation can be found in a publicly disclosed presentation authored by Equistar chemicals<sup>3</sup>, given as exhibit D.

The Schombourg et. al. patent (U.S. 6,448,343) which is cited against this patent application claims a thermoplastic composition containing maleic anhydride which is then reacted with (the amino portion of) an aminosilane compound. The silane end groups are later reacted with one another to form a "crosslinked" structure.

Because the maleic anhydride group is consumed in the reaction step with the aminosilane compound, there is no longer a maleic anhydride reaction site for the bonding reactions as those described above (e.g., reaction with nylon or EVOH).

Therefore, the composition claimed by Schombourg would have no ability to function as an adhesive that this application is directed to.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1002 of Title 18 of the United States Code, and that such willful false statement may jeopardize the validity of the application or any patent issued thereon.

By:   
Mark. S. Pucci

Date: 1-3-05

## INTRODUCTION OF TIE LAYERS IN COEXTRUSION

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### ABSTRACT

The use of anhydride modified resins as tie-layers in coextruded multilayer applications is discussed. Tie-layer resins are used to adhere two resins that otherwise would have poor adhesion. A review of the factors effecting adhesion and how they relate to tie-layer performance is discussed. Methods for evaluating tie-layers are discussed including testing methods and guidelines. Processing guidelines for extrudable adhesives are provided.

### INTRODUCTION

Coextrusion allows a processor to take advantage of various attributes of resins in order to achieve the best overall product. In cases where the desired resins do not adhere to each other, it is necessary to use a tie-layer. Tie-layer resins are chemically modified polyolefins used in coextrusion or coating operations to bond two dissimilar materials together that otherwise would have poor adhesion to each other. For example, a multilayer product combining the properties of EVOH (low oxygen permeability) and HDPE (stiffness) can be produced using tie-layers. Tie-layer resins are used in a variety of applications such as extrusion coating, blown and cast film, blow molding, extrusion lamination, sheet, thermoforming and other specialty processes.

Anhydride modified polyolefins and ethylene copolymers are capable of chemically reacting with nylon, paper, some metals and EVOH to provide excellent adhesion. Anhydride modified resins (AMR) are also used with resins such as polyesters where the increased polarity compared to unmodified polyolefins can result in improved adhesion. This paper provides guidelines on how to evaluate and use AMR tie-layer resins in multilayer applications.

### FACTORS EFFECTING ADHESION IN COEXTRUSION

AMR can react with EVOH and nylon to form strong bonds [1] while still maintaining adhesion to polyolefins. Adhesion can be effected by several factors [2, 3]. Table 1 shows the effect of process variables on adhesion. For a given tie-layer, increasing the melt contact time usually increases adhesion since the reaction is more complete. Contact time is affected by processing variables such as chill roll temperatures, line speed and die design.

Table 1. The effect on peel strength by increasing the given variable.

An increase in:	Effect on peel strength
EVOH ethylene content	▲
Graft content	▲
Melt contact time	▲
Melt temperature	▲
Tie layer thickness	▲
Orientation	▼
Thermoforming draw ratio	▼
Blow-up ratio	▼
Line speed	▼

Higher melt and die temperatures generally improve adhesion since the rate of reaction and diffusion (i.e., chain entanglement) is accelerated. Figure 1 shows that increasing the heat seal temperature increases the adhesion

strength of modified EVA to nylon 6. While higher temperatures generally improve adhesion, it is important not to exceed the recommended processing temperatures due to potential processing problems, gel formation or even resin degradation. EVA resins are more sensitive to degradation compared to polyolefins and should not be processed above 450°F. AMR tie-layers are typically processed at 400-450°F but can be processed as high as 620°F under controlled conditions. Thermal stability of the tie-layer will depend on both time and temperature in the extruder.

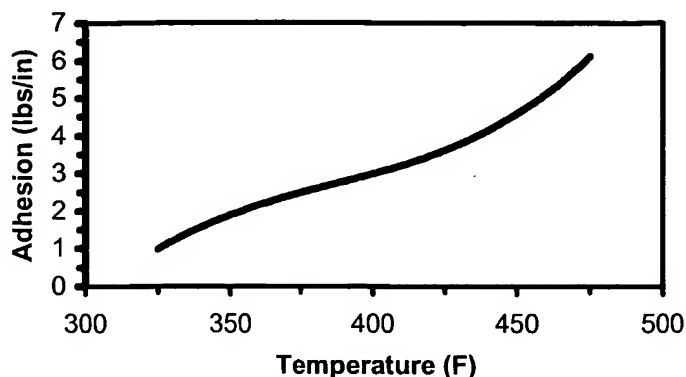


Figure 1. Lamination of 9% EVA tie-layer to nylon-6 at various temperatures

The thickness of the tie-layer also affects adhesion. Increasing the thickness of the tie-layer increases the amount of graft and the amount of material available to absorb energy. Figure 2 shows the beginning of the plateau region for a modified LLDPE tie-layer at higher thicknesses. At thinner gauges, adhesion increases rapidly as a function of thickness as shown for an unmodified LLDPE tie-layer. Therefore, not using enough tie-layer could result in adhesion failures. It is critical to test products under the most extreme conditions including potential variations in processing temperature or tie-layer thickness.

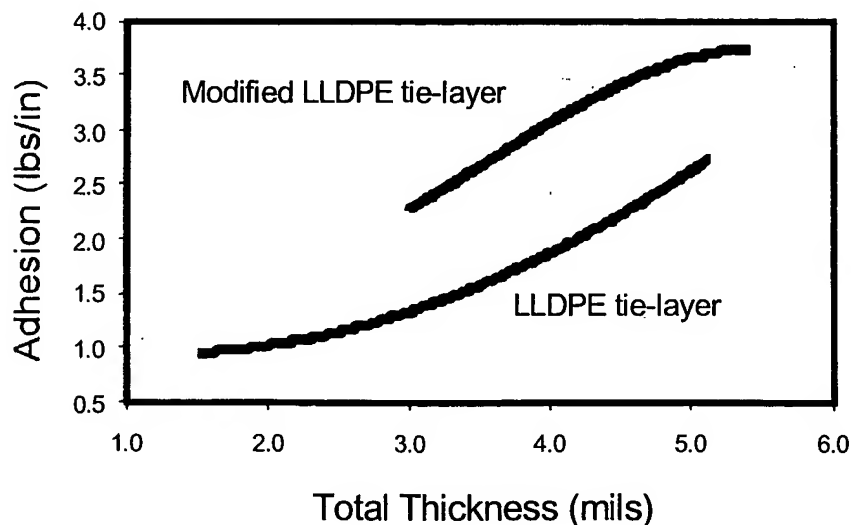


Figure 2. Effect of total film thickness on adhesion for a coextruded cast film with a structure of HDPE/Tie/EVOH/Tie/HDPE and a layer distribution of (36/8/12/8/36) for two LLDPE tie-layers.

The application process can also effect adhesion as high interfacial stress can lead to lower adhesion. Orientation during or after processing (e.g., thermoforming) increases interfacial stress, reduces the number of reaction sites per unit area and decreases the tie-layer thickness leading to a decrease in adhesion.

The properties of the resin will also effect adhesion. Figure 3 shows the adhesion strength of various LLDPE tie-layer resins in a cast film structure. This difference in adhesion performance between these LLDPE tie-layer resins can be attributed to the overall physical properties of the resin and the level of functionality.

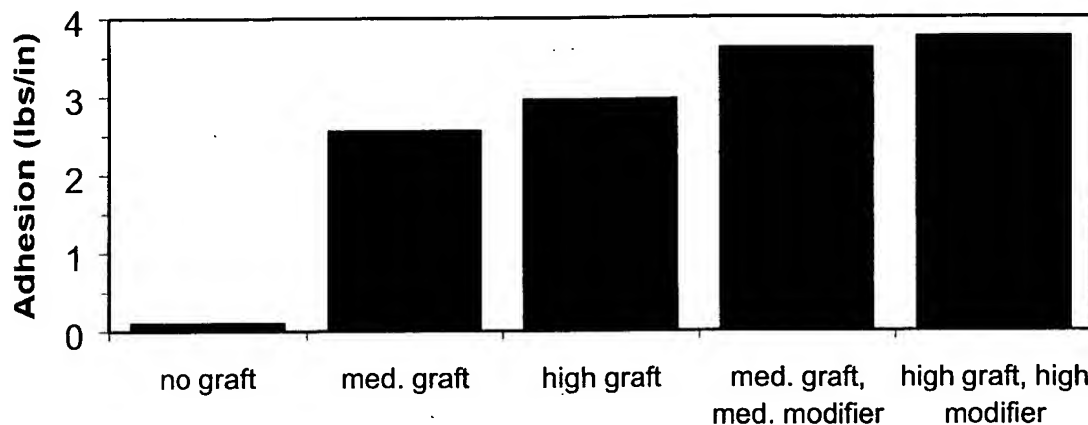


Figure 3. Various LLDPE tie-layers in cast film with a structure of HDPE/Tie/EVOH/Tie/HDPE, a layer distribution of 36/8/12/8/36 and a total thickness of 5 mils.

#### WHEN IS A TIE-LAYER REQUIRED?

A tie-layer is needed when the substrates do not adhere to each other. The most prevalent barrier resins, EVOH and nylon, do not bond well to PE but do bond well to each other. Therefore, a tie-layer is not needed between EVOH and nylon. Typically, polyolefins and ethylene copolymers bond well to each other, therefore a tie-layer is not needed between EVA and LLDPE. New barrier resins such as liquid crystalline polymers (LCP) and polyketone (PK) do not bond well to AMR since the anhydride does not react with the carbonyl group.

Table 2. Adhesion of various resins to anhydride modified resins.

	Anhydride Modified LLDPE	Anhydride Modified EVA
PE	***	***
EVOH	***	***
Nylon	***	***
Ionomer	**	**
Acrylonitrile	*	**
PP	*	**
PET	*	**
PEN	*	**
PC	*	**
PUR	*	**
PS	*	**
LCP	*	*
PK	*	*

\* = no adhesion, \*\* = moderate adhesion, \*\*\* = excellent adhesion

LCP – liquid crystalline polymer, PET – polyethylene terephthalate,

PK – polyketone, PUR – thermoplastic polyurethane, PS – polystyrene,

PE – polyethylene, PC – polycarbonate, EVOH – ethylene vinyl alcohol

## TESTING METHODS

It is essential to know how the tie-layer performs. One measure of tie-layer performance is peel strength [4]. Peel strength is reported as the force required to separate a sample per specimen width. Conversions for different reported adhesion units are shown in Table 3. The typical width of a sample strip is 1 inch. Variables for adhesion testing include testing speed, test configuration, aging time, structure, and size of sample. It is important that results only be compared for samples with one variable change.

Table 3. Unit conversions for adhesion testing.

Multiply by factor to convert from ▼	lbs/in	g/cm	N/mm	g/15 mm	N/25.4 mm
lbs/in	--	179	0.175	268	4.45
g/cm	0.00560	--	$9.81 \times 10^{-4}$	1.50	0.0249
N/mm	5.71	1020	--	1530	25.4
g/15 mm	0.00373	0.667	$6.54 \times 10^{-4}$	--	0.0166
N/25.4 mm	0.225	40.1	0.0393	60.2	--

Initiating of the films is critical when measuring adhesion. Several steps can be taken to improve results. One option is to orient the films. Orientation decreases the adhesion and allows for initiation. Another method is to use a stiffer resin. An analogy can be made to the sharpness of a notch. A blunt crack tip will not propagate as easily as a well defined notch. Therefore HDPE can often be substituted in place of LDPE or LLDPE to make the films easier to evaluate.

Most peel strength testing is conducted using a 180° "T-peel." In order to get accurate results, it is important that the film not elongate during testing. Elongation will contribute to the measured force which is will be higher than the actual peel strength.

Figure 4 shows the adhesion after several days. Adhesion initially increases as a function of time. Therefore, it is important to compare samples that have been aged for the same amount of time. Samples can be initiated right away, but it is recommended to wait at least 72 hours before determining peel strength.

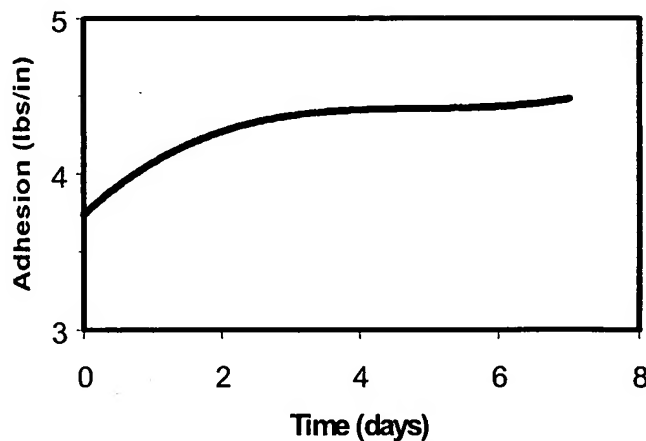


Figure 4. Peel strength as a function of time for a five-layer film of HDPE/tie/EVOH/tie/HDPE.

## EVALUATING TIE-LAYER PERFORMANCE

In addition to peel strength, field performance is generally conducted. The tie-layer resin should be selected based on the resins being bonded. For example, an AMR tie-layer resin is going to provide minimal benefit for adhering polyolefins to each other. Also, a tie-layer resin that performs well for one substrate may or may not perform well with a different substrate. The processing conditions, any secondary operations (e.g., orientation or thermoforming) and the end-use environment will all effect the performance of the tie-layer resin. It is imperative that the conditions most likely to cause adhesion failures are identified. These conditions may occur during orientation, retort, thermoforming or during use by the consumer.

In order to evaluate a tie-layer resin the following information is needed:

- Peel strength
- Economics
- Final product properties
- Processing
- Regulatory requirements
- Field performance

The minimum adhesion should be determined by measuring adhesion under the most severe conditions and including a safety factor. Maximum adhesion results in using a thicker tie-layer or a higher performance resin than what is needed which are both costly alternatives. Any regulatory requirements, such as those of the Food and Drug Administration (FDA), must also be identified. The effect on the properties of the final product should be considered. The tie-layer resin that is often thought of as simply an adhesive can effect machinability, clarity and physical properties such as puncture, stiffness and moisture vapor transmission rate (MVTR). For example, a HDPE tie-layer will have higher stiffness and lower MVTR than a comparable EVA but with lower clarity.

Figure 5 shows a comparison of MVTR values for various tie-layer resins. HDPE has high crystallization which gives good chemical resistance and better thermal resistance than LDPE. However, the high degree of crystallization results in higher shrinkage compared to other polyolefins that can lead to lower adhesion due to high stress at the interface. Therefore, HDPE tie-layer resins are typically used in combination with HDPE resins. For film applications, LLDPE tie-layer resins are increasingly popular due to a good combination of physical properties and processability.

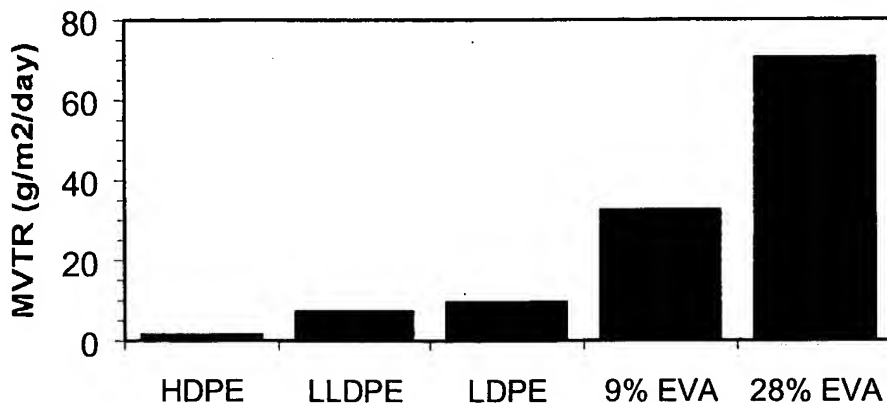


Figure 5. MVTR of various tie-layer resins.

Processability is usually measured in terms of output, backpressure and extruder amps. Most tie-layer resins will process similarly to the base resin. Aesthetics of the film can be effected by a rheological mismatch. The layers in contact should have similar viscosities; otherwise, flow instabilities can lead to waviness or poor layer distribution [5, 6]. Furthermore, the interior layer should have the highest viscosity, while the skin layer should have the lowest viscosity. Simply matching the melt index may not always be sufficient but is a good starting point. EVOH is not as shear thinning at PE, so at high shear rates it would be necessary to use resins with a different melt index. For example, cast film produced with a structure of LDPE/Tie/EVOH/Tie/LDPE and melt indices of 6/2/4/2/6 results in flow instability seen as non-uniform layer distribution and parabolic flow lines. By changing the melt index of the EVOH from 4 g/10 min to 2.4 g/10 min, the cast film quality is acceptable.

Aesthetics can also be effected by gels. An improper shutdown can lead to significant gel issues. A shutdown should be done using a resin other than the tie-layer such as LDPE. Typically, an extruder should not be allowed to idle more than 30 minutes when containing the tie-layer and even then a small amount of throughput is recommended. Purge compounds have been designed specifically for EVOH and nylon, but these compounds should be purged prior to shutdown or idling of the extruder.

## SUMMARY

Extrudable adhesives can be used in a variety of coextrusion processes to adhere dissimilar materials to produce a number of end-use products with the desired attributes. The selection of the tie-layer resin is important to the overall performance of the package and the processor should consider all conditions of use and desired properties. Tie-layer resins should be evaluated based on peel strength, field performance, processability, aesthetics, regulatory requirements, and economics to identify the resins that gives the overall best value to the processor. The processor who evaluates a tie-layer resin simply based on the lowest cost resin or highest adhesion possible may be missing cost savings. Therefore, it is recommended that processing and performance requirements be reviewed early in the package development process to find the optimal resin for a given application.

## ACKNOWLEDGMENT

The author would like to thank the Performance Products group for their assistance.

## REFERENCES

1. Botros, M. G., *TAPPI 1995 PLC Proceedings*, TAPPI Press, p. 331.
2. Morris, B., *TAPPI 1996 PLC Proceedings*, TAPPI Press, p. 191.
3. Zimmerman, D. and Ward, D. in *Extrusion Coating Manual*, 4<sup>th</sup> edn. TAPPI Press, 1999, p. 249.
4. Pucci, M., Jachec, K., Machonis, J., et al., *J. Plast. Film Sheet*, 7: 24 (1991).
5. Kirkland, C., *Plast. Tech.*, p. 58 (Feb. 1983).
6. Schrenk, W. and Veazey, E., in *Encyclopedia of Polymer Science and Engineering*, Vol. 7, Wiley & Sons, 1985, p. 106.



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► [Products : Adhesive Resin](#)

## ► **ADMER®** Adhesive Resin



ADMER® Adhesive Resin is a modified polyolefin with functional groups, designed to bond to a variety of polyolefins, ionomers, polyamides, ethylene vinyl alcohol (EVOH), polyesters (PET), polycarbonates, polystyrenes and metals such as steel and aluminum. ADMER serves as a tie-layer in unique multi-layer structures to combine properties of different materials, such as gas barrier resins and moisture barrier resins. Available in pellet form, ADMER can be used in a wide variety of coextrusion processes for bottles, tubes, sheets and films.

Based on your required adhesion performance, processing conditions and other requirements, Mitsui can promise a solution to meet your needs.

- ☒ [Introduction](#)
- [Characteristics](#)
- [Applications 1](#)
- [Applications 2](#)
- [Charts](#)

► [Product Contact](#)

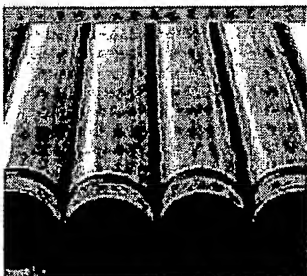
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EXHIBIT B TO PUCCI AFFIDAVIT

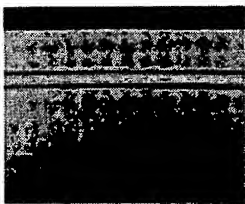
## ► **ADMER®** Adhesive Resin



### Characteristics

#### Strong Adhesion

ADMER® adheres, by thermal reaction, to Nylon (Ny), EVOH, polystyrene (PS), polyesters (PET, PETG), polycarbonate (PC), polyolefins (PP, PE) and metals such as steel and aluminum.



Cross-section of Multi-layered Sheet  
(PP/ADMER/EVOH/ADMER/PP)

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#### Adhesion Durability and Polyolefin-like Properties

Its mechanical strength, heat resistance and chemical resistance properties distinguishes ADMER and enables the compound to be boiled, hot filled and retorted.

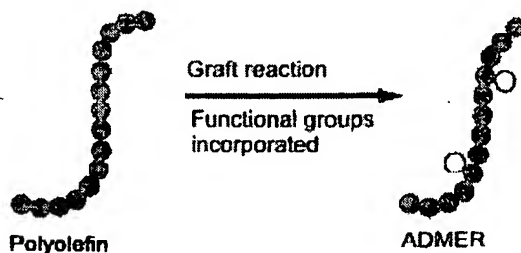
#### Easy Processing

ADMER, a thermoplastic, can be processed easily by:

- coextrusion blow molding
- tube coextrusion
- sheet coextrusion
- film coextrusion (cast and blown film)
- coextrusion coating
- powder coating (metal coating)
- co-injection

#### FDA Status

ADMER complies with 21 CFR 175, 105. PP based ADMER complies with 21 CFR section 177, 1390, (C) (2) under certain conditions.



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Products : Adhesive Resin

## ► ADMER® Adhesive Resin



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### Applications

#### Structure (Outside «—)

**Bottle** PP/AD/EVOH/AD/PP

Ketchup, Mayonnaise, Jelly Chocolate, Barbecue Sauce, Relish, Salad Dressing

PC/AD/EVOH/AD/PP

Ketchup, Infant Formula

HDPE/AD/EVOH/AD/EVOH

Orange Juice

HDPE/AD/Ny

Agrochemical

HDPE/AD/EVOH

Solvent

**Tube**

LDPE/AD/Ny

Cosmetic

LDPE/AD/Ny/AD/LDPE

LDPE/AD/EVOH/AD/LDPE

Medical

**Cup,  
Tray**

PS/AD/EVOH/AD/PE

PS/AD/EVOH/AD/PP

Pudding

PP/AD/EVOH/AD/PP

Apple Sauce, Pasta/Entree

**Film**

Ny/AD/LDPE (LLDPE)

Ny/AD/EVA

Processed Meat

LDPE/AD/Ny/AD/LDPE

Cheese

LDPE/AD/EVOH/AD/LDPE

Bag In Box, Meat

Ny/EVOH/AD/LLDPE

Stretch Shrinkable Film

Ny/EVOH/AD/EVA

(Meat/Processed Meat)

**Pipe**

EVOH/AD/X-PE  
EVOH/AD/PB-1 (PP)

Floor Heating Pipe

PE/AD/Steel

Oil-Pipe, Natural-Gas Pipe

Steel/AD

Water-Pipe

X-PE/AD/Aluminum

Aluminum Sheathe

# series 3000

## Introduction

The Bynel™ CXA 3000 series of resins was created to provide good bonding in structures designed to use polyamide (nylon) and ethylene vinyl alcohol gas barrier resins with polyethylene, ethylene copolymers, Surlyn® ionomer resins, polypropylene, polycarbonate, and polyester sealing or structural layers.

## Adhesion Mechanism

All of the resins in the CXA 3000 series are ethylene copolymers containing anhydride functionality. The ethylene backbone contributes extrudability, and the ester comonomer gives us the required polymer to polymer wetting in the melt stage so essential to obtaining good bonding between dissimilar resins. Anhydride functionality is built into the CXA 3000 series resins to promote a coupling reaction between the adhesive resin and the polyamide (nylon) or ethylene vinyl alcohol gas barrier resins. In the case of polyamides, the anhydride reacts with the amine ends forming an amide linkage as depicted in Figure 1. With ethylene vinyl alcohol, an ester linkage is possible by the reaction of the anhydride with the hydroxyl groups of the alcohol. This is shown in Figure 2.

## Processing Temperature

Anhydride-containing resins are readily subject to hydrolysis converting the anhydride to the acid form as noted in Figure 3. The coupling reactions noted above are more likely to occur and do so at a much more rapid rate with the anhydride rather than its acid form. Therefore, it is important to be sure sufficient heat energy is present during coextrusion processing to reverse the hydrolysis reaction. Testing shows that at

a melt temperature below 200°C the conversion to the active anhydride form proceeds slowly. At 200°C, the conversion is essentially complete in about five (5) minutes, and at 240°C the conversion time is estimated to be one to two minutes. The suggested processing temperature for each CXA 3000 series resin grade is detailed on its individual bulletin contained in the pocket of the folder. These temperature profiles are suggested based on optimizing the melt temperature for maximum adhesion without exceeding each resin's degradation temperature.

## Grades

The Bynel™ CXA 3000 series of resins is still expanding. As we develop new grades, they are initially given "E" numbers (example, CXA E-148). When fully commercial, these experimental grades are given their series number by adding the first two digits of the series number to the last two digits of the experimental number (example, CXA 3048). This CXA 3000 series folder may contain data sheets on both commercial and developmental (E) grades. Availability of the developmental grades is noted on the individual data sheets and can also be verified by contacting your local Du Pont representative or his office.

The technical data contained herein are guides to the use of Du Pont resins. The advice contained herein is based upon tests and information believed to be reliable, but users should not rely upon it absolutely for specific applications since film and adhesion properties will vary with processing conditions. It is given and accepted at user's risk and confirmation of its validity and suitability in particular cases should be obtained independently. The Du Pont Company makes no guarantee of results and assumes no obligation or liability in connection with its advice. This publication is not to be taken as a license to operate under, or recommendation to infringe, any patents.

Figure 1  
ANHYDRIDE/AMINE (H<sub>2</sub>N)  
COUPLING

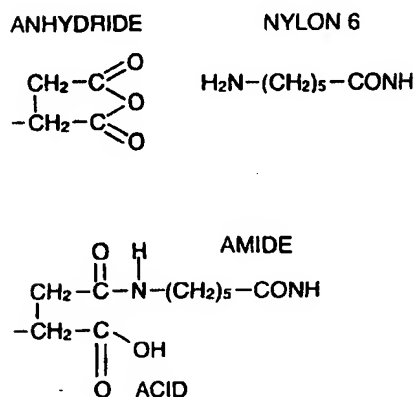


Figure 2  
ANHYDRIDE/HYDROXYL(OH)  
COUPLING

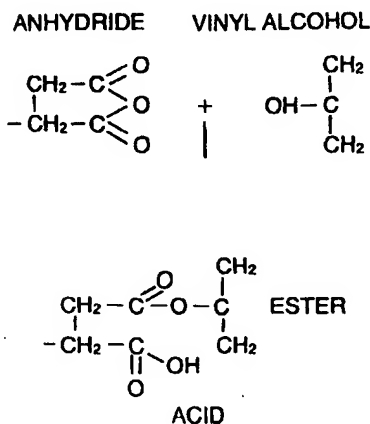
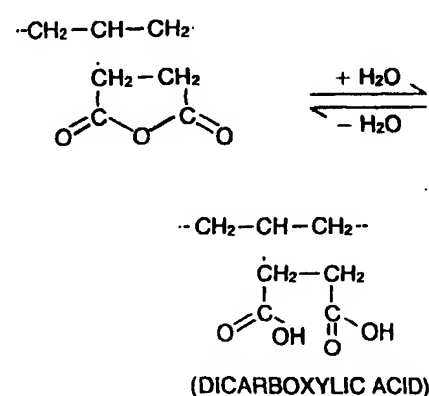


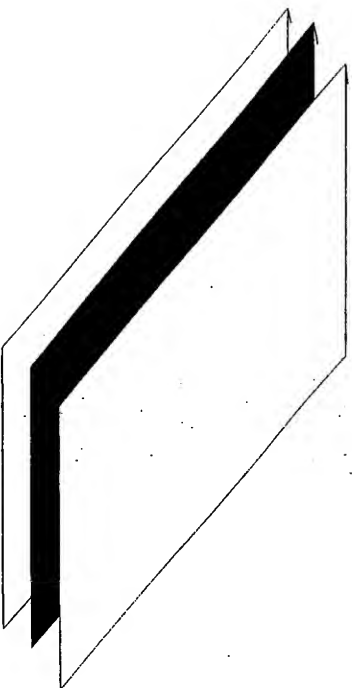
Figure 3  
ANHYDRIDE HYDROLYSIS



# Improved Clarity EVA Based Plexar

Daniel Ward

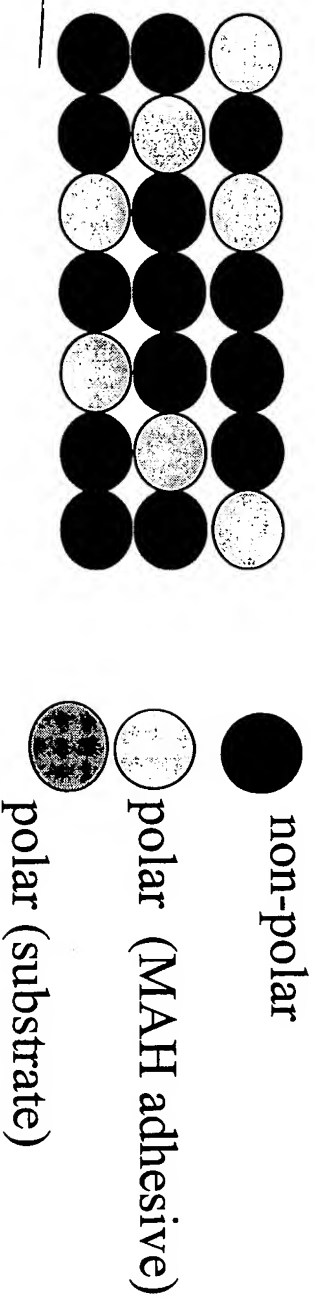
Equistar Chemical Company



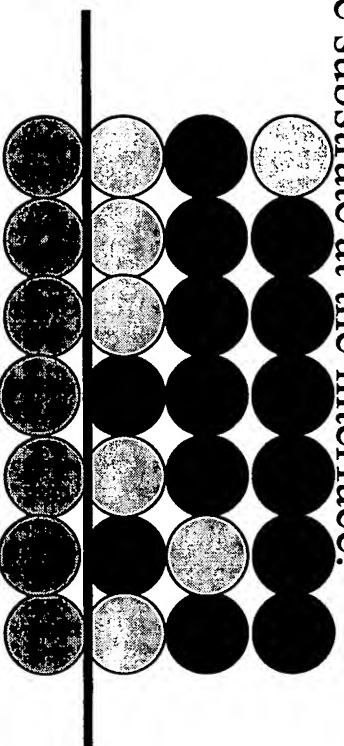
**EQUISTAR**

# Tie-resin Bonding Mechanism

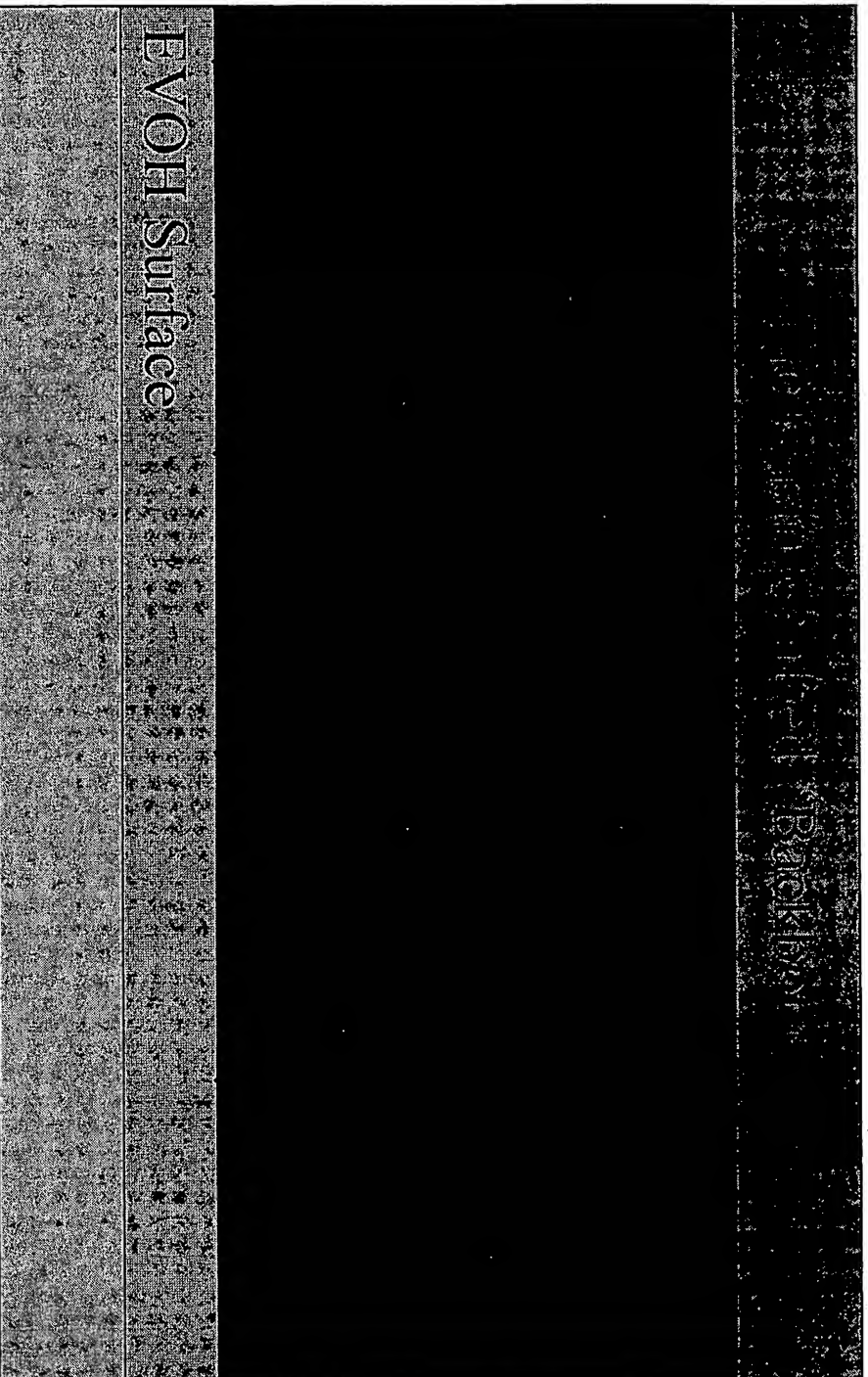
Before extrusion polar groups (functionality) are randomly distributed in resin:



In melt phase, polar groups migrate to barrier material interface and bond with the substrate at the interface:



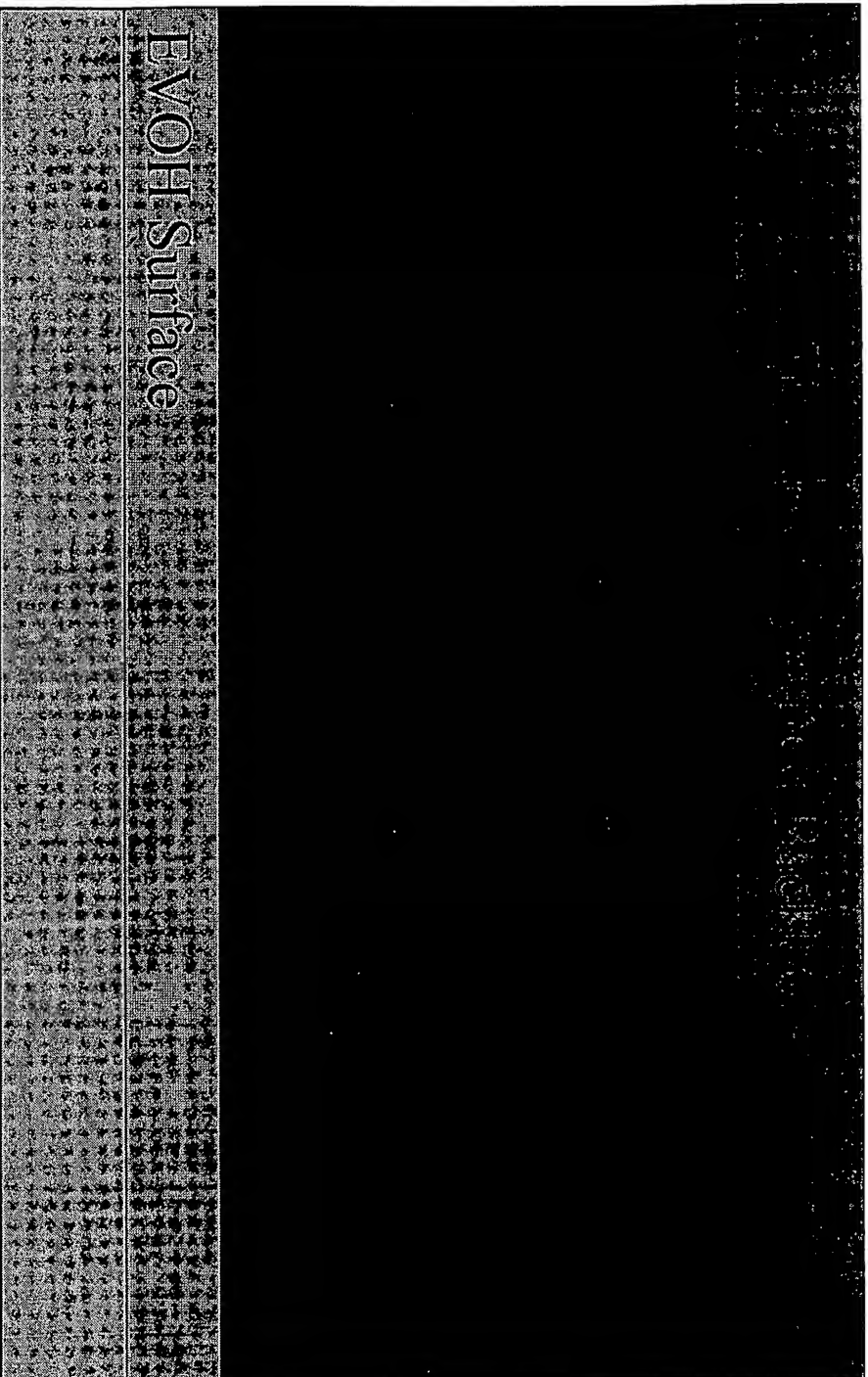
# Chemical Interactions



EVOH Surface

**EQUISTAR**

# Chemical Interactions



EVOH Surface

**EQUISTAR**



# Tie-layer Bonding Chemistry

EVOH:

Anhydride + Hydroxyl  $\Rightarrow$  Ester + Carboxylic

Nylon:

Anhydride + Amine  $\Rightarrow$  Amide + Carboxylic

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